

INFRARED LINE PARAMETERS AT LOW TEMPERATURES RELEVANT TO PLANETARY ATMOSPHERES

PRASAD VARANASI

Institute for Atmospheric Sciences, State University of New York at
Stony Brook, NY 11794-2300

ABSTRACT

Employing the techniques that we have described in several of our publications for measuring infrared lineshifts, linewidths and line intensities with a tunable diode laser, we have measured these parameters for lines in the important infrared bands of several molecules of interest to the planetary astronomer at low temperatures that are relevant to planetary atmospheres using He, Ne, Ar, H₂, N₂, O₂, and air as the perturbers. In addition to obtaining the many original data on the temperature dependence of the intensities and linewidths, we were also the first to measure the same for the collision-induced lineshift of an infrared line and to show that it was markedly different from that of the corresponding collision-broadened linewidth.

INTRODUCTION AND BRIEF PRESENTATION OF DATA

The parameters describing absorption due to infrared lines of planetary atmospheric molecules are the position, intensity, half-width, lower level energy and the collision-induced lineshift. In the modelling of planetary atmospheres based upon comparison of the observed and calculated planetary spectra, data on the above mentioned infrared line parameters at the relevant atmospheric temperatures would be needed. (Even though the position and the energy level are independent of the temperature of the gas, often in spectra involving hot bands measurements performed at several low temperatures are useful in assigning these two parameters to a line unambiguously.) This need is the primary reason for performing the measurements that have been reported by our laboratory for nearly two decades. To the best of our knowledge, most of the measurements reported in Refs. 1-12 are the first ever

published on the accurate magnitudes as well as the temperature dependence of these parameters. We are the first ever to have measured the temperature dependence of collision-induced lineshifts of any molecule in the infrared at low temperatures. We have used He, Ne, Ar, H₂, N₂, O₂ and air as the gases perturbing the radiative process. Lines formed in the atmospheres of the major planets are broadened predominantly by H₂ and, to a lesser degree, by He. In the atmosphere of Titan, a satellite of Saturn with an atmosphere composed mostly of N₂ and exhibiting CH₄ spectra, N₂-broadening is important. There have been some suggestions, if not indications, recently that Ar might be present in Titan's atmosphere in amounts sufficient to make Ar-broadening also relevant. N₂, O₂ and air were chosen with the terrestrial atmospheric application in mind. Ne was used only in lineshift measurements in an attempt to examine the relationship between the observed lineshifts in the case of the noble gases and of their polarizabilities.

Our tunable diode laser spectrometer, the other necessary equipment, the experimental procedure, and the low temperature absorption cell used in the present studies have been described by us previously.¹⁻⁴ The techniques employed for measuring lineshifts, linewidths and intensities have been described in considerable detail by us in Refs. 5, 6, and 7 respectively. We also discussed in detail in Refs. 5-12 the errors to be assigned to the data that we obtained.

This space is too short for a meaningful presentation and discussion of the many data of interest to the planetary astronomer that we have obtained in our laboratory in recent years. The References that we provide at the end of this paper should serve the reader just as well in learning about these data. However, the data that we have measured most recently on the 13.7 μm lines of C₂H₂ have not yet been published and are presented in an abbreviated form in Tables 1 and 2. The parameter n in Table 1 defines the power law dependence of the collision-broadened linewidth upon temperature.⁴

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Table 1. Collision-broadened line widths in the 13.7 μ Band of $^{12}\text{C}_2\text{H}_2$.

Broadener	Line	ν (cm^{-1})	γ_L^0 ($\text{cm}^{-1} \text{atm}^{-1}$)			n
			295 K	206 K	174 K	
H_2	P(11)	703.2556	0.0926 \pm 0.0020			0.75
	P(8)	710.3198	0.0942 \pm 0.0015	0.1169 \pm 0.0036		
	R(7)	747.9624	0.0928 \pm 0.0017	0.1228 \pm 0.0028	0.1370 \pm 0.0042	
	R(18)	773.7435	0.0851 \pm 0.0016			
	R(19)	776.0810	0.0851 \pm 0.0033	0.1247 \pm 0.0006	0.1055 \pm 0.0025	
	R(21)	780.7532	0.0852 \pm 0.0007		(250 K)	
Broadener	Line	ν (cm^{-1})	γ_L^0 ($\text{cm}^{-1} \text{atm}^{-1}$)			n
			295 K	206 K	145 K	
N_2	P(11)	703.2556	0.0871 \pm 0.0020			0.77
	P(8)	710.3198	0.0937 \pm 0.0006	0.1246 \pm 0.0031		
	R(7)	747.9624	0.0937 \pm 0.0009	0.1200 \pm 0.0014	0.1617 \pm 0.0013	
	R(18)	773.7435	0.0772 \pm 0.0015			
	R(19)	776.0810	0.0756 \pm 0.0007	0.1018 \pm 0.0032		
	R(21)	780.7532	0.0704 \pm 0.0008			

Table 2. Absolute Intensities, S_J ($\text{cm}^{-2} \text{atm}^{-1}$), and Collision-Broadened Line Widths, γ_L^0 ($\text{cm}^{-1} \text{atm}^{-1}$), in the $13.7 \mu\text{m}$ Band of $^{12}\text{C}_2\text{H}_2$ at 294 K.

Line	ν (cm^{-1})	S_J ($\text{cm}^{-2} \text{atm}^{-1}$)	γ_L^0 ($\text{cm}^{-1} \text{atm}^{-1}$)		
			He	Ar	air
P(11)	703.2556		0.0479 ± 0.0018	0.0597 ± 0.0011	
P(8)	710.3198	3.76 ± 0.06	0.0553 ± 0.0020	0.0708 ± 0.0026	0.0980 ± 0.0034
R(7)	747.9624	16.64 ± 0.25	0.0463 ± 0.0007		0.0897 ± 0.0006
R(18)	773.7435	2.54 ± 0.08	0.0465 ± 0.0013	0.0473 ± 0.0002	
R(19)	776.0810		0.0455 ± 0.0007		
R(21)	780.7532	4.49 ± 0.05	0.0442 ± 0.0006	0.0462 ± 0.0009	

The absolute intensities reported by Varanasi et al., [*JQSRT* **30**, 497 (1983)] and later adapted into the GEISA and AFGL's HITRAN Data Bases are 3.72, 16.68, 2.50 and 4.38 for the P(8), R(7), R(18) and R(21) lines, respectively.

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